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14. ABSTRACT

Poly-p-phenelenebenzobisoxazole (PBO, commercial name ZylonTM, Toyobo Co.)is one of the rigid-rod polymers which produces fiber with excellent mechanical properties. This polymer, originally developed by the U.S. Air Force to replace metals in space and aviation applications1, is currently one of the more promising materials for fibers used in personnel ballistic armors. In this study we evaluate the degradation mechanisms of PBO fibers and investigate strategies to stabilize them using supercritical CO2 as an extraction medium, a transport medium, and a polymerization medium. Various treatments and their effects are reported herein.

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Final Report on evaluation of rigid-rod polymeric fibers by post-treatment in scCO2

ABSTRACT

Poly-p-phenelenebenzobisoxazole (PBO, commercial name ZylonTM, Toyobo Co.)is one of the rigid-rod polymers which produces fiber with excellent mechanical properties. This polymer, originally developed by the U.S. Air Force to replace metals in space and aviation applications1, is currently one of the more promising materials for fibers used in personnel ballistic armors. In this study we evaluate the degradation mechanisms of PBO fibers and investigate strategies to stabilize them using supercritical CO2 as an extraction medium, a transport medium, and a polymerization medium. Various treatments and their effects are reported herein.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

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Walsh, P. J., Cunniff P., Lesser A. J. (2006) Environmental Effect on poly-p-phenylenebensobisoxaxole fibers II., Attempts at Stabilization, J. Appl. Polym. Sci. 102(4):3819-3829.

Hu, X.B., Lesser, A. J. (2006) Solid state processing of polymers in the presence of supercritical carbon dioxide, J. of Cellular Plastics, 42(6):517-527.

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A. J. Lesser, Effects of scCO2 treatment on the short-term and long-term tenacity in PBO fibers, Natick Soldier Center, August 2005

A. Lesser, P. Walsh, Mechanical vs Chemical Degradation in PBO fibers, Fall CUMIRP Meeting, Oct. 2005

P. Walsh, Physical and Chemical degradation in PBO fibers, Gordon Composite Conference Poster presentation, Ventura CA, Jan. 2006

A. J. Lesser Strategies of stabilization using scCO2 on PBO fibers update , Fall Spring CUMIRP Meeting, Univ. of Mass., May 2006

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Walsh, P.J., Lesser, A.J. (2006) Mechanisms and Alleviation of PBO fiber degradation, 64th Annual Technical Conference, Society of Plastics Engineers, 2057-2061

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NAME	PERCENT_SUPPORTED	
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K. Best	1.00	
FTE Equivalent:	**2.00**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED	
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FTE Equivalent:	**0.20**	
Total Number:	**1**	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Alan Lesser	0.06	No
FTE Equivalent:	**0.06**	
Total Number:	**1**	

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Peter Walsh

Total Number: 2

Names of personnel receiving PHDs

<u>NAME</u>
Peter J. Walsh

Total Number: 1

Names of other research staff

<u>NAME</u>   <u>PERCENT_SUPPORTED</u>

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Stabilization of Poly-p-phenylenebenzobisoxazole Fibers

Introduction

In our previous progress report the mechanisms of degradation of PBO AS fiber due to exposure to moisture, acidic environments and UV-Visible light (UV-Vis) were investigated in detail [1]. The mechanism of degradation for moisture was found to be primarily physical in nature. The loss in properties was accompanied by an increase in the size of voids within the fiber while ATR-FTIR spectroscopy revealed no chemical changes near the fiber surface. Exposure to strong acids in aqueous environments appeared to accelerate the separation of the fibrils within a fiber together with subsequent diminishments in tenacity. This suggests that any residual phosphoric acid present may contribute to degradation by moisture through its affinity with water by enhancing moisture adsorption or by a chemical reaction affecting small amounts of material at the surface of individual fibrils.

In contrast to the degradation due to moisture, the effect of UV-Vis radiation was found to be chemical in nature. This form of degradation is most likely due to the intrinsic photo-reactivity of the PBO polymer due to its highly conjugated chemical structure and π-π stacking within PBO crystals [2]. It should be noted that fibers exposed to concentrated phosphoric acid and subsequently exposed to UV-Vis radiation showed an increased loss of strength with higher concentrations indicating that there is a synergistic effect when both a challenging acid species and UV-Vis radiation are present.

The observation that strength is decreased by swelling of the fibrillar structure of the fiber and the increase in size and/or number of defects actually presents us with an opportunity to increase initial fiber strength through the application of forces that tend to compact the fiber structure and decrease the number and size of defects present. Because of the chemical structure of the PBO backbone there are no secondary chemical forces acting between the basic fibrillar structural elements of the fiber. Once a compacting force has been applied introduction of a secondary inter-fibril force that could maintain the compacted morphology and provide load transfer between fibrils might be beneficial both in terms of increasing initial fiber tenacity, compressive strength and resistance to degradation of strength by moisture.

Having a general concept of the degradation pathways for moisture, acidic environments and UV-Vis radiation, we propose some approaches to alleviate fiber degradation [3].

Super-Critical Fluid Extraction of Phosphoric Acid

Given that the presence of acid accelerates both degradation by moisture and UV-Vis radiation, extraction of residual phosphoric acid should improve fiber environmental stability. Super critical carbon dioxide has frequently been employed as an extraction medium due to its combination of low viscosity and negligible surface tension [4]. Herein, we investigate the use of super critical carbon dioxide ($scCO_2$) to directly wash the residual phosphoric acid out of the fiber.

A related approach investigated involves using $scCO_2$ as a transport medium to introduce the low molecular weight compounds pyridine, morpholine and trimethyl

phosphate in an effort to neutralize the residual acid, and potentially solubilize it in $scCO_2$ for subsequent extraction.

UV-Vis Blockers

For polymeric materials, a common method for improving weathering resistance or photo-stability is through the use of additives. During photo-oxidation, absorption of a photon by the polymer produces an activated species followed by a photophysical and chemical conversion of the activated species [5]. Therefore, various additives such as a UV reflector, a UV absorber, an excited-state quencher, or a free-radical scavenger and/or hydroperoxide decomposer have been long used in industry [6,7,8] to mediate UV-Vis degradation. The approach investigated herein involves coating of PBO fibers with different UV reflectors or absorbers, which are named UV blockers here. The UV blockers used are carbon black, exfoliated graphite, and a glassy TiO_2 created using sol-gel chemistry [9, 10,11].

Compaction

Several approaches to densify the fiber microstructure were undertaken. The first involves applying a twist to single fibers. Twist has long been known to improve the strength of staple fiber materials. It is also used in continuous yarn systems to force the assembly of single fibers to behave as a contiguous unit. It is well known that PBO fibers have a nano-fibrillar structure, which is very similar to that of spun yarns made from staple fiber except that it occurs over a different length scale [12, 13]. Generally, for yarns made from staple fibers, the strength shows a maximum while the extension to break continually increases with degree of twist [14, 15]. A second approach is to apply hydrostatic pressure to the fiber in an $scCO_2$ environment with the intent to compact the fiber microstructure and allow the plasticizing ability of scCO to aid in the reduction of defects. Finally fibers were exposed to high temperature, tension and hydrostatic pressure in a $scCO_2$ environment simultaneously. The idea was to use the tension to orient the fiber elements more perfectly and allow the heat and $scCO_2$ to reduce the number and size of defects present.

PBO Polysiloxane composites

Prevention of swelling of the PBO AS fiber by moisture and maintenance of externally imposed compaction of the fiber morphology should have the effect of increasing the fiber's initial tenacity and resistance to degradation by moisture. The introduction of inter-fibrillar stabilizing forces has previously been studied with the aim of improving the low transverse mechanical properties of LC rigid rod polymers; Approaches include infiltration of the fiber with a high modulus glassy filler [16, 17], infiltration with an organic polymer phase during the coagulation step of the spinning process [18], creation of an interpenetrating rigid rod fibril-amorphous polymer network by spinning a fiber from a solution containing both a LC rigid rod polymer and an amorphous organic polymer [19, 20] and cross-linking the material in adjacent fibrillar regions [21, 22].

The work undertaken in this research differs from the previous studies in that it is not primarily aimed improvement of fiber transverse mechanical properties but instead at improving the environmental stability of PBO AS fiber by introduction of inter-fibrillar

adhesive forces. In addition, rather than altering the nature of the spinning process this work is toward post-spinning processes applicable to stabilization of commercially produced PBO fiber. Toward this end composites of PBO AS fiber and polysiloxanes crosslinked in a hydrosilation reaction have been prepared in super-critical carbon dioxide environment [23] according to Scheme 1. This approach takes advantage of the high solubility of siloxanes in $scCO_2$ by introducing relatively small molecular weight vinyl substituted polysiloxane prepolymer and hydride containing crosslinker to the fiber, swelling the fiber with the siloxane prepolymer and subsequently initiating crosslinking by introduction of a Karstedt's catalyst known to be highly soluble and robust in a $scCO_2$ reaction environment. The intent is that the resulting elastomeric PDMS will infiltrate the fiber, adhere to the fibrillar elements and provide a secondary force to prevent expansion of the fiber microstructure. Fiber impregnation with two resin systems were investigated: a low molecular weight vinyl substituted polydimethylsiloxane prepared by polycondensation (PVMS), and Sylgard 184 a commercially available PDMS system produced by Dow Corning Corp.

Experimental

Materials

PBO AS Fiber

The as-spun PBO AS fiber used was Zylon AS, which was supplied by US Army Soldier System Command at Natick, MA. The related properties of the fiber can be found in reference [24].

Extraction and Neutralization of Phosphoric Acid

Morpholine, pyridine and trimethylphosphate were purchased from Aldrich and used as received.
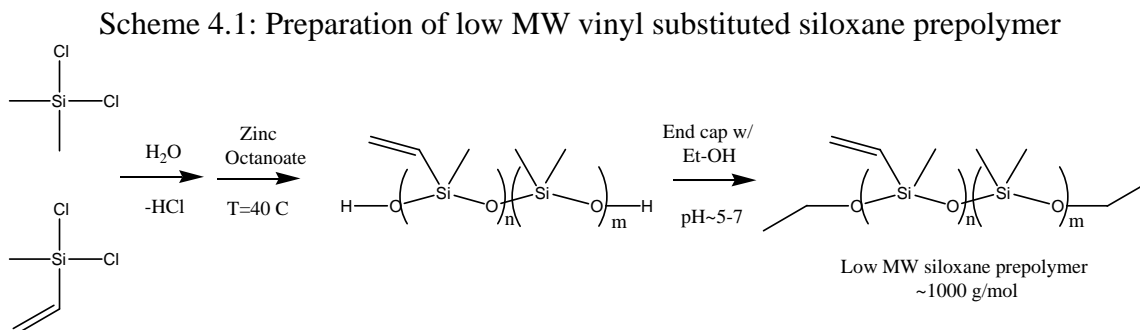
UV-Vis Blockers

Expanded graphite was supplied by Prof. Lawrence T. Drzal in Michigan State University. Carbon black is Black Pearl 800 provided by Cabot Corp. Glassy titanium dioxide was prepared from a sol-gel using titanium isopropoxide precursor in solution with absolute alcohol both purchased from Sigma-Aldrich and used as received.

Polymethylvinylsiloxane-polydimethylsiloxane Prepolymer (PVMS)

Polymethylvinylsiloxane-polydimethylsiloxane resin was prepared in a condensation reaction from dichlorodimethylsilane and dichloromethylvinylsilane in an aqueous solution at room temperature according to scheme 1. After completion of the initial condensation reaction the majority of the aqueous phase was removed, zinc acetate was added and the solution heated to 45 °C to reduce cyclic content and increase molecular weight. The product was then washed in absolute ethanol to end cap active chain ends and remove the remaining hydrochloric acid byproduct of the condensation reaction. The resulting vinyl substituted PDMS resin was combined with an appropriate quantity of 1,2,5,7-tetramethylcyclotetrasiloxane crosslinker (D4^H) such that there was a 1:1 equivalence of resin vinyl functionality and crosslinker hydrides. The reactants

reactants used in preparation of the resin were purchased from Sigma-Aldrich and used as received. The D4^H crosslinker was purchased from Gelest Corp. and used as received.

Scheme 4.1: Preparation of low MW vinyl substituted siloxane prepolymer

Sylgard 184 Polydimethysiloxane Resin

Sylgard 184 Elastomer Base is a product of Dow Corning Corp. It is composed of 60 or more wt. % dimethylvinyl terminated polydimethyl siloxane, 30-40 wt. % dimethylvinylated and trimethylvinylated silica and 1-5 wt % tetra(trimethylsiloxy)silane and 0.7 wt % xylene.

Sylgard 184 Polydimethylsiloxane Crosslinker

Sylgard 184 Curing Agent is a product of Dow Corning Corp. It is composed of 40-70 wt % Methylhydrosiloxane-dimethylsiloxane copolymer.

Methods

Super-Critical Carbon dioxide Extraction

Fiber washing was carried out in a custom-made high-pressure vessel designed to allow the circulation of CO_2. The details of this experimental apparatus are shown in Figure 4.1. In order to not damage or disturb the alignment of the fiber tows during washing, bundles of fiber approximately 12 inches in length were supported to an aluminium frame first, followed by insertion into the high-pressure vessel. A pressure regulator was used to control the CO_2 flow rate. Samples were washed in the vessel at fixed temperatures and pressures with different times. After washing, the temperature was allowed to drop and the vessel was depressurized slowly. Washed PBO fibers were used for mechanical testing, elemental analysis and weathering experiments.
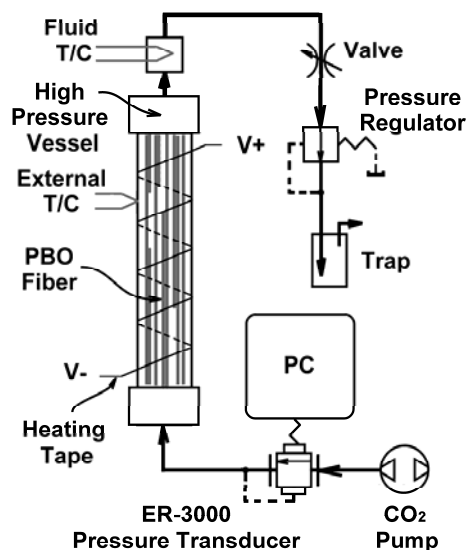
Figure 4.1: Schematic of device used for super-critical CO_2 extraction of residual phosphoric acid.

Preparation of PBO AS/Crosslinked PDMS Composites in scCO2

Soaking and crosslinking of PBO AS/Crosslinked PDMS composites was carried out in the custom built device illustrated in Figure 4.2. A CO_2 pump supplied high pressure CO_2. The ER-3000 pressure transducer/controller was used to pressurize the removable high pressure reaction vessel and to ramp pressure down after the completed reaction. Once pressurized the reaction vessel was placed in an oven to attain the desired temperature and final pressure.

Figure 4.2: Schematic of the device used in preparing PBO AS/Crosslinked PDMS composites in a super-critical carbon dioxide environment. The high-pressure reaction vessel is removed after pressurization with CO_2 and placed in an oven to maintain temperature and pressure above the critical point.

UV-Vis Exposure

Uv-Vis exposure procedures and equipment are identical to those described in our previous progress report.

UV-Vis Spectroscopy

UV-Vis spectra were collected using an Hitachi U-3010 spectrophotometer in transmission mode

Tensile Testing

Tensile testing procedures and equipment are identical to those described in our previous progress report.

SEM

Scanning Electron Microscopy equipment and procedure are identical to those described in our previous progress report.

ATR-FTIR

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy equipment and procedures are identical to those described in our previous progress report.

SAXD

Small Angle X-Ray Diffraction Equipment and procedures are identical to those described in our previous progress report.

Elemental Analysis

Elemental Analysis equipment and procedures are identical to those described previously.

MALDI-TOF

MALDI spectra were acquired using a Reflex III MALDI-TOF (Bruker Daltonics) spectrometer. For MALDI analysis polysiloxane prepolymer resin was dissolved in a 10mg/mL solution with THF and applied to a stainless steel target in a matrix of 2-5-Dihydroxybenzoic acid.
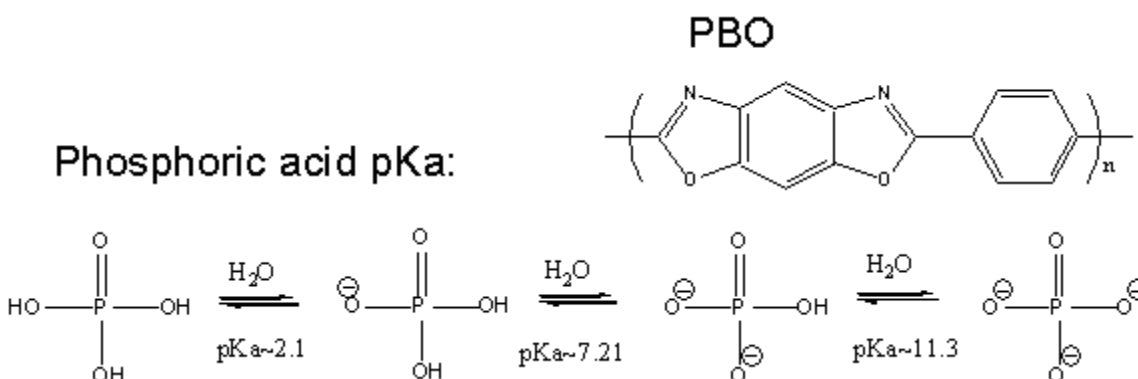
NMR

^{1}H NMR spectra were collected using a Bruker DPX 300 instrument using $CDCl_3$ solvent.

Results and Discussion

Extraction of Residual Phosphoric Acid in Super-Critical Carbon Dioxide

   In the work previously described in Chapter 3, elemental analysis indicated that an amount of residual phosphorus ranging between 0.3 – 0.4 wt% resides in the PBO AS fiber inferring the presence of residual phosphoric acid (PA). With exposure to an aqueous environment hydrolytic reactions with the weakly basic oxazole ring may cause disruption of the ring structure or chain scission . The pKa values for each phosphoric acid proton loss and the backbone structure of PBO are shown in Scheme 4.2.

Scheme 4.2: pKa values for dissociation of phosphoric acid protons

   In an effort to extract the residual PA, PBO AS fiber was washed in supercritical carbon dioxide ($scCO_2$) at various conditions of temperature, pressure and $scCO_2$ flow rate using the device illustrated in Figure 4.1. Elemental analysis was subsequently used to measure changes in the quantity of residual phosphorus. The results presented in Table 4.1 show that as flow rate and temperature are increased, $scCO_2$ can remove part of the residual phosphoric acid in the fiber but cannot remove it completely. The concentration of residual phosphorus can not be decreased below approximately 0.25 wt%-0.3 wt% suggesting that the highly crystalline PBO AS fiber may be only partially permeable to CO_2.

Table 4.1: Weight percentage of residual phosphorus remaining in PBO AS fiber washed in $scCO_2$ under varying conditions of temperature, pressure.

T (°C)	P (psi)	Q (Lpm)	wt% residual PA
Control	Control	Control	0.4
50	2500	5	0.4
100	2500	5	0.3
100	2500	10	0.25
100	5000	10	0.25

Single fiber tensile testing was used to assess the effect of washing in $scCO_2$ on mechanical properties. Figure 4.3 compares the tenacity of neat PBO AS fiber to fibers washed at a flow rate of 5 LPM, temperature of ~100 °C and pressure ranging from 2500 psi to 5000 psi. Exposure to $scCO_2$ does not appear to have a detrimental effect on the strength of the fibers. In fact, at pressures of 2500 and 3250 psi there appears to be a trend toward increase in fiber properties. This will be discussed further in this chapter's section on improving fiber mechanical properties via compaction of the fiber morphology. In addition, the SEM images of Figure 4.4 show that the surfaces of $scCO_2$ washed fibers are relatively unchanged as compared to pristine control fiber. The UV-Vis light stability of $scCO_2$ washed fibers was also evaluated. Figure 4.5 shows the single fiber tensile testing results for fibers exposed at 750 W/m^2 over a 300 hour duration. The response of the neat fiber and the washed fiber is identical. This result supports the idea presented in Chapter 3 in which it is supposed that UV-Vis degradation is not primarily related to the presence of residual phosphoric acid but is instead due to the intrinsic photo-reactivity of the highly conjugated structure of PBO.
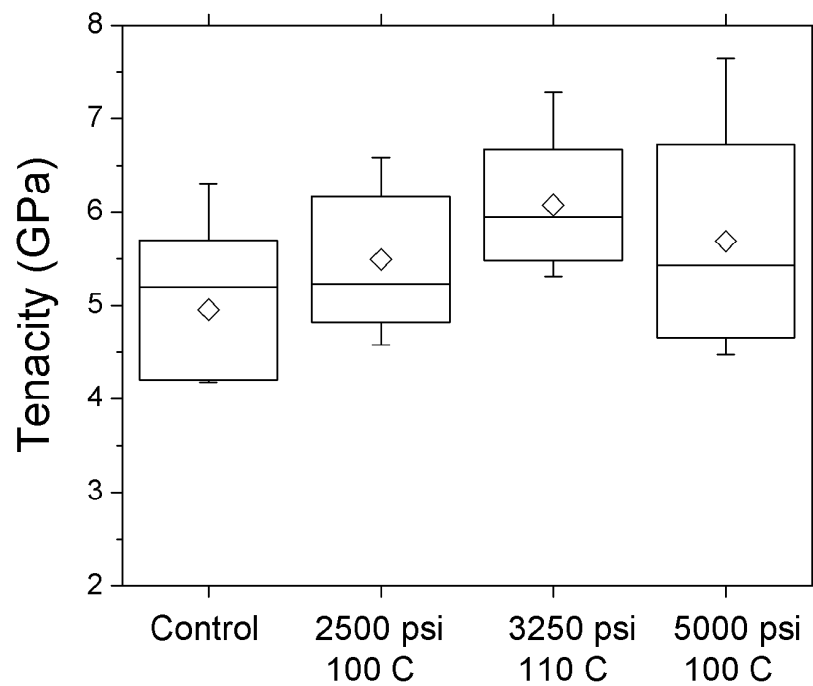
Figure 4.3: Tenacity of PBO AS fibers washed with scCO2 at 5 LPM flow rate and varying conditions of temperature and pressure compared to pristine control fiber. Whiskers denote minimum and maximum, box denotes median and standard deviation and the open diamond denotes the mean.
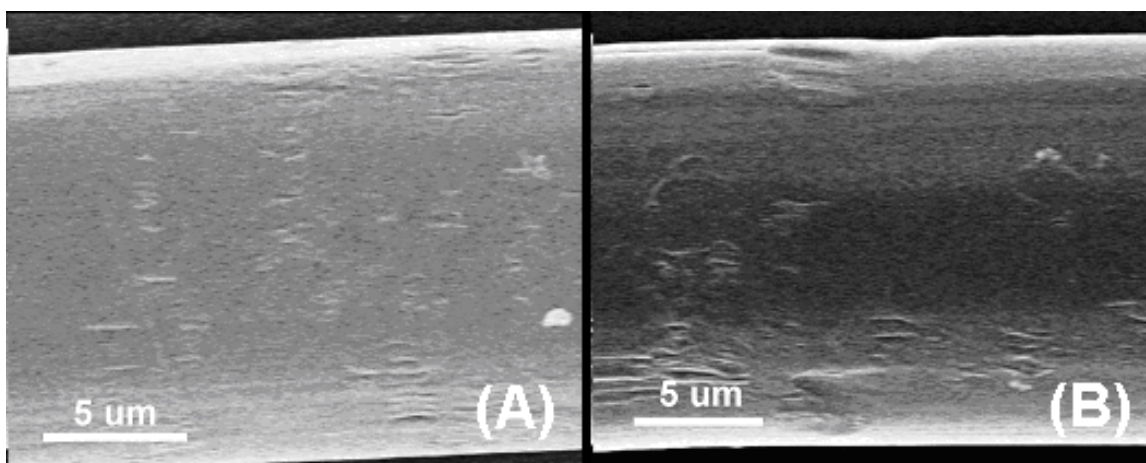

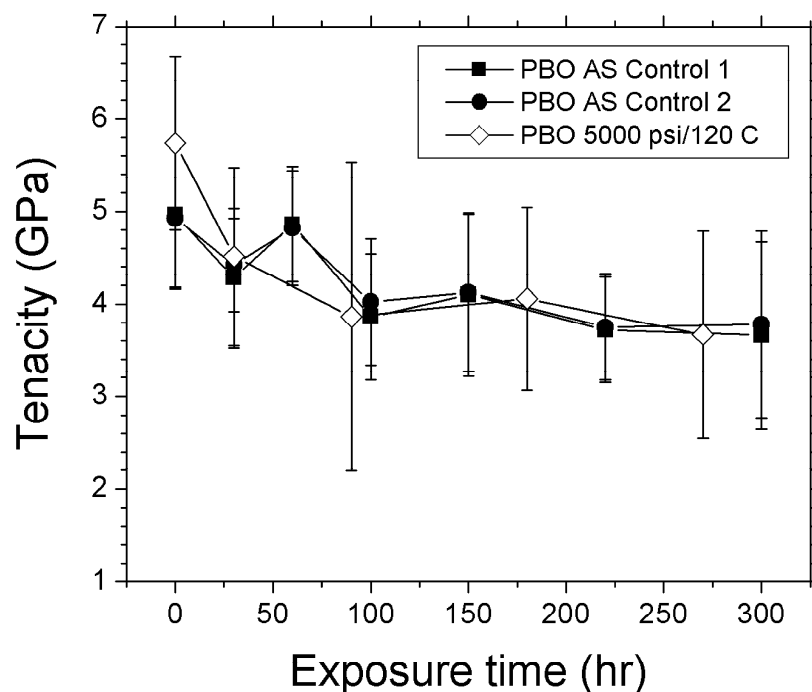Figure 4.4: SEM of scCO2 washed PBO AS fiber (A) compared to control fiber (B).

Figure 4.5: Tenacity of scCO2 washed PBO AS fibers exposed to UV-Vis light at 750 W/m^2 compared to pristine control fiber.

Neutralization and Extraction of Residual Phosphoric Acid

A second approach to improving the stability of PBO in aqueous conditions was to neutralize any residual phosphoric acid with a small molecule having a more favorable reaction with phosphoric acid than the polymer backbone. An scCO$_2$ environment could be used to both enhance introduction of the small molecule and extract the neutralized phosphoric acid.

Three low molecular weigh compounds shown in scheme 4.3 were selected to explore this hypothesis. Morpholine (MOR) and pyridine (PYR) were chosen based on their pKa values relative to the pKa values for loss of phosphoric acid hydrogens (scheme 1). Trimethylphosphate (TMP) was selected because it has a chemical structure very close to phosphoric acid and has been shown in other polymers to actually work as a molecular fortifier due to noncovalent interactions between the polar phosphate and polymer network [25]. For these experiments PBO fiber was soaked in scCO$_2$ at 100 °C/5000 psi for 30 hours then immersed in 100% concentrations of each compound at room temperature for approximately 160 hours. The mechanical properties were initially tested and additional samples were exposed to UV-visible light and subsequent mechanical properties tested.

Scheme 4.3: Small molecules used to treat PBO AS fibers: pyridine, morpholine and trimethyl phosphate.
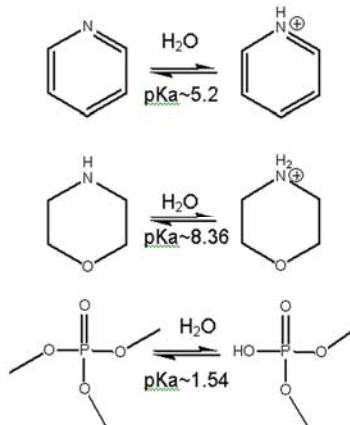

Figure 4.6 compares the effect these compounds have on the initial fiber tenacity and the indication is that there are no changes in tenacity relative to the control fiber. However, as shown in Figure 4.7, exposure to all three of these compounds negatively affects the UV-Vis stability. Both trimethylphosphate and pyridine exposed fiber showed slightly less stability than the control fiber – in fact the response of these two compounds is similar in magnitude to that for fiber exposed to concentrated phosphoric acid (Chapter 3, Figure 3.8). After only 30 hours the morpholine treated samples had degraded to the extent that it was not possible to test single fibers.

Information published by Toyobo [24] and work by Allen et al. on the chemically and morphologically similar poly(p-phenylenebenzobisthiazole) fibers [26] has already indicated decrease in the tenacity of PBO with exposure to strong acids and bases, however, the results of the present work are alarming in that here comparatively weak acids and bases in combination with exposure to UV-Vis light have been observed to significantly degrade fiber strength.
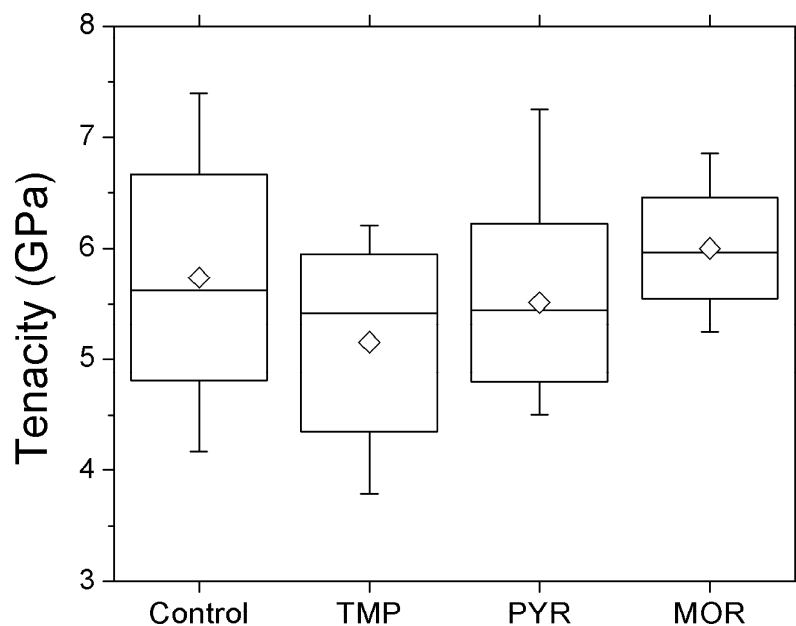
Figure 4.6: Comparison of initial tenacity for control PBO AS fiber and fiber treated with trimethyl phosphate (TMP), pyridine (PYR) and morpholine (MOR). Whiskers denote minimum and maximum, box denotes median and standard deviation and the open diamond denotes the mean.
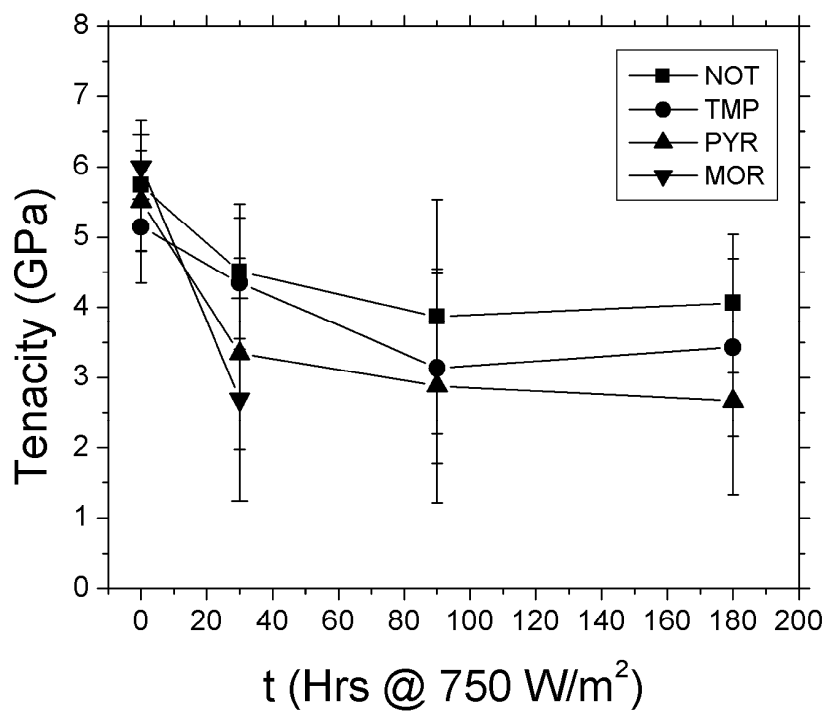

Figure 4.7: Tensile testing results for PBO AS fibers treated with pyridine, morpholine and trimethyl phosphate.

In further work PBO AS fibers were exposed to pyridine in an $scCO_2$ environment. The idea here was to more effectively introduce pyridine into the fibrillar bundle and where it could neutralize the residual acid and subsequently be extracted along with the $scCO_2$ upon depressurization. Figure 4.8 shows the UV-Vis stability of these fibers plotted along with that of two control samples and the pyridine exposed sample of Figure 4.7. The primary point of interest is that the $scCO_2$/Pyridine sample shows approximately similar response to UV-Vis light as the control groups. This is in contrast to the decrease in UV-Vis stability of the PBO fibers exposed to pyridine without $scCO_2$ of Figure 4.7. One explanation for the UV-Vis stability of the pyridine/ $scCO_2$ exposed fiber is that the $scCO_2$ environment is an effective extraction solvent for removing pyridine without damaging the fiber.
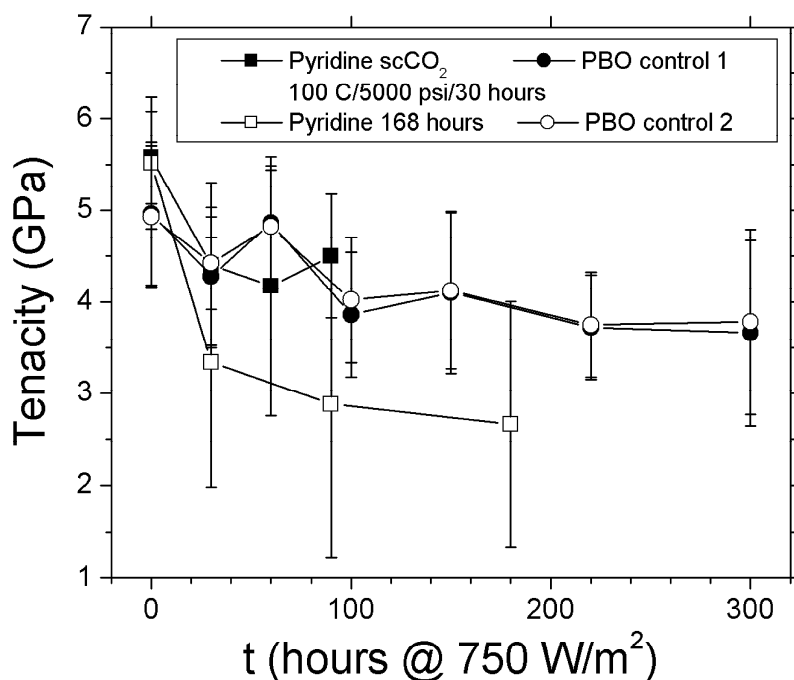

Figure 4.8: Tensile testing results for PBO AS fibers treated with pyridine in a scCO2 environment.

Figure 4.9 shows the ATR-FTIR spectra for fibers exposed to liquid water, and treated with 1 M phosphoric acid, 100% trimethyl phosphate, 100% pyridine and 100% morpholine. While the spectra for the pristine fiber and water exposed fiber are similar and indicate little or no chemical change near the fiber surface, changes are observed for fibers exposed to the phosphoric acid, trimethyl phosphate, pyridine and morpholine. In the case of phosphoric acid exposed fiber a broad peak develops between ~3200 and 3300 cm^{-1}. This peak is assigned to a secondary amine on the oxazole ring nitrogen implying some hydrolytic reaction, but because there is no accompanying carbonyl peak the oxazole ring is probably not disrupted. Exposure to trimethyl phosphate shows evolution of a narrow peak at ~1700-1800 cm^{-1} that is ascribed to a carbonyl. The

pyridine exposed fiber shows development of both an oxazole ring secondary amine peak between ~3200-3300 cm^{-1} and a narrow carbonyl peak at ~1700-1800 cm^{-1}. The morpholine exposed fiber shows the appearance of a narrow peak at ~1690 cm^{-1} that is thought to be due the formation of an amide carbonyl, however there is no accompanying secondary amine peak. It is not possible to deduce the exact chemical pathway of these degradation reactions from these spectra. Taken together they suggest that hydrolytic reactions originating at the oxazole nitrogen and subsequent alteration or disruption of the oxazole ring around its quaternary carbon center are the most likely route [3].

All the above results were somewhat surprising. Since it was initially anticipated that the residual phosphoric acid played a key role in at least accelerating the degradation of the PBO, and the introduction of a base should neutralize the acid. Nonetheless, the reduction of fiber tenacity with UV-Vis exposure shows that the stability of PBO fiber in the presence of UV-visible light spectrum radiation is highly sensitive to the environment and any condition either basic or acidic (Chapter 3 concentrated phosphoric acid exposure) can accelerate the degradation. This observation seems to support the hypothesis proposed in Chapter 3 that the PBO fiber may be intrinsically susceptible to photodegradation. A recent study by Wang et al. shows that these polymers do absorb significant amount of energy in the UV-visible spectrum [2]. It should be emphasized that absorption of energy doesn't necessarily indicate instability. However, energy is absorbed nonetheless and, if these fibers are intrinsically unstable in this spectral range, the presence of either an acid or base may synergistically increase the degree of degradation.
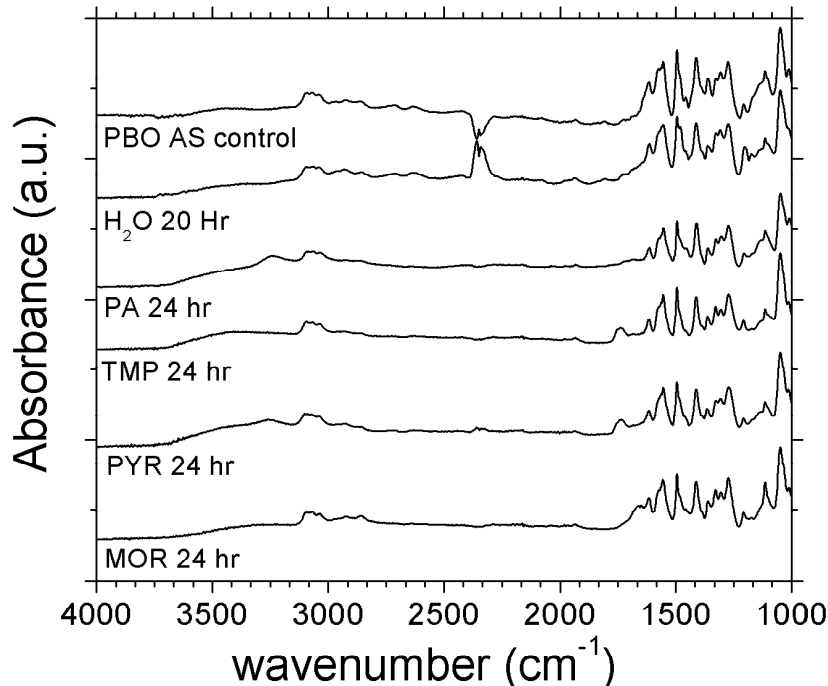

Figure 4.9: ATR-FTIR spectra of PBO AS fibers treated with phosphoric acid, pyridine, morpholine and trimethyl phosphate compared to spectra of pristine fibers and water exposed fibers.

UV-Vis Blockers

Both the conjugated structures in PBO chains and the π - π stacking in crystals may make PBO fibers intrinsically photo-sensitive. For polymeric products, a frequent method of improving weathering resistance or photo-stability is through the use of additives to absorb incident UV-Vis radiation. In this work UV blockers applied to the PBO AS fibers were carbon black, exfoliated graphite (EG) and glassy titanium dioxide prepared via a sol-gel method.

Both carbon black and the exfoliated graphite flakes were pulverized using an ultrasonic processor in ethanol for 24 hours. PBO fiber bundles were immersed in the sonicated solution, taken out and dried for UV-visible light exposure, and subjected to tensile testing. SEM images of PBO fibers coated with carbon black and graphite are shown in Figure 4.10.

Note that exfoliated graphite does not cover the fiber surface in a consistent manner. Although the thickness of exfoliated graphite is in the range of nanoscale, the aspect ratio of graphite is much larger and this prevents defect free coating of the fiber. In contrast, carbon black powder does cover the surface of the fiber fairly well. There are at least two reasons for better coating of carbon black. One is that the size of a carbon black particle is about 20 to 50 nm and their agglomeration is still in the range of a few hundreds of nanometers. The other reason is that carbon black has polar groups such as -C=O, -COOH and –OH near the particle surface. Compared to exfoliated graphite, these polar groups have stronger interactions with PBO fiber, which will result in better coating and coating strength.
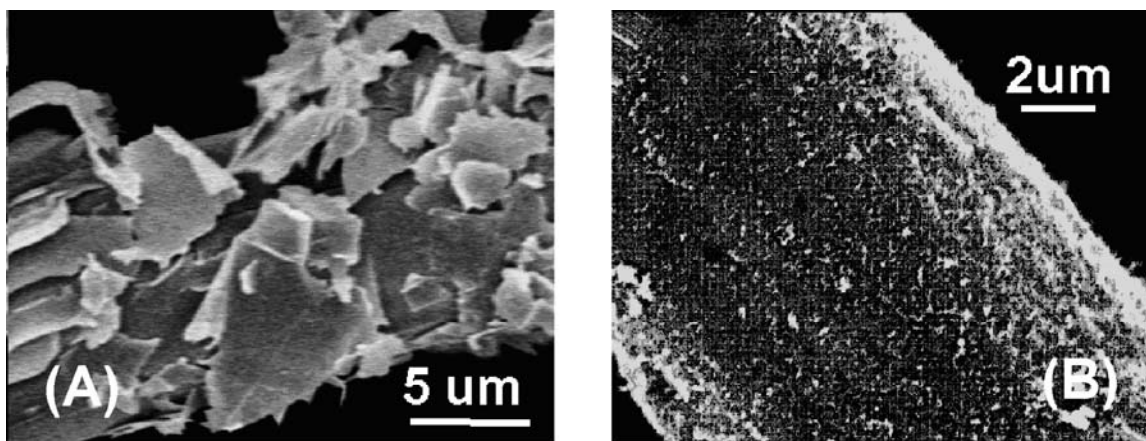

Figure 4.10: SEM of (A) graphite and (B) carbon black coated PBO AS fibers.

As shown in Figure 4.11, the load-at-break of carbon black coated fibers is very close to those of control samples at the same UV-Vis exposure time. Coating PBO fiber with carbon black does not appear to increase the light stability of PBO fibers. In contrast to carbon black, it seems that exfoliated graphite increases the rate of UV-Vis degradation of PBO fibers. In Figure 4.11, the load-at-break of EG coated fibers decreases more quickly compared to uncoated ones. Carbon black coating does not increase the light stability of PBO fibers. One possible reason is that the coating may be

too thin to block the UV-visible light. The exact thickness of coating is not clear from SEM images.

A third UV-Vis blocking material used is a glassy coating of TiO_2 created using sol-gel chemistry. A sol-gel was made by adding titanium isopropoxide to ethanol with pH brought to ~2 using dilute hydrochloric acid [9, 10, 11]. Previously prepared PBO AS single fiber tensile specimens were dipped in the sol-gel and allowed to dry in vacuum at 50 °C for one hour. Figure 12 shows the UV-Vis absorbance of the sol-gel and the dry TiO_2 film. While the wet sol-gel blocks most of both the UVB and UVA spectrum, the glassy TiO_2 film is only effective in blocking the UVB wavelengths. Figure 4.13 shows an SEM image of the resulting glassy TiO_2 coating. The coverage appears very consistent, with thickness on the order of 100s of nanometers. However, there are some cracks and defects evident. The cracks aligned with the fiber axis are due to contraction of the glassy TiO_2 as the ethanol solvent evaporates away, while those perpendicular to the fiber axis result from the fracture of the glassy and brittle coating due to handling the fibers after evaporation. The Figure 4.11 tensile testing results for samples exposed to UV-Vis show that the tenacity of the TiO_2 coated fibers is nearly identical to that of two uncoated control groups. Again, it is a surprise that this coating does not enhance the UV-Vis stability. This could be due to either inadequate film thickness or defects in coverage due to cracking during drying and handling. Also, given that the TiO_2 film only absorbs strongly in the UVB spectrum, UVA spectrum radiation may still be reaching the fiber surface.

These results, although unsuccessful in improving the resistance of PBO fiber to UV-Vis spectrum radiation, clarify some of the attributes needed for successful application of a UV-Vis blocking material. The blocker must efficiently either absorb or reflect incident UV-Vis radiation over the full UV spectrum. The coating must completely cover the fiber surface and be flexible enough that bending of the fibers does not result in fracture or other defect. Given the results for degradation due to physical expansion of the fibrillar bundle with exposure to water presented in chapter 3 it would be advantageous if the coating also excluded water from the fiber interior.
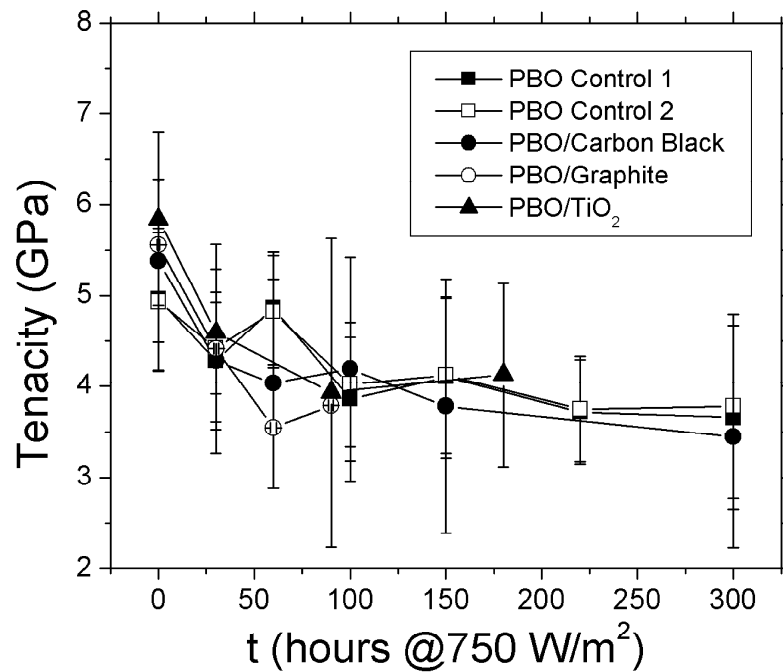
Figure 4.11: Tensile testing results for carbon black, graphite and TiO2 coated fibers exposed to UV-Vis light.
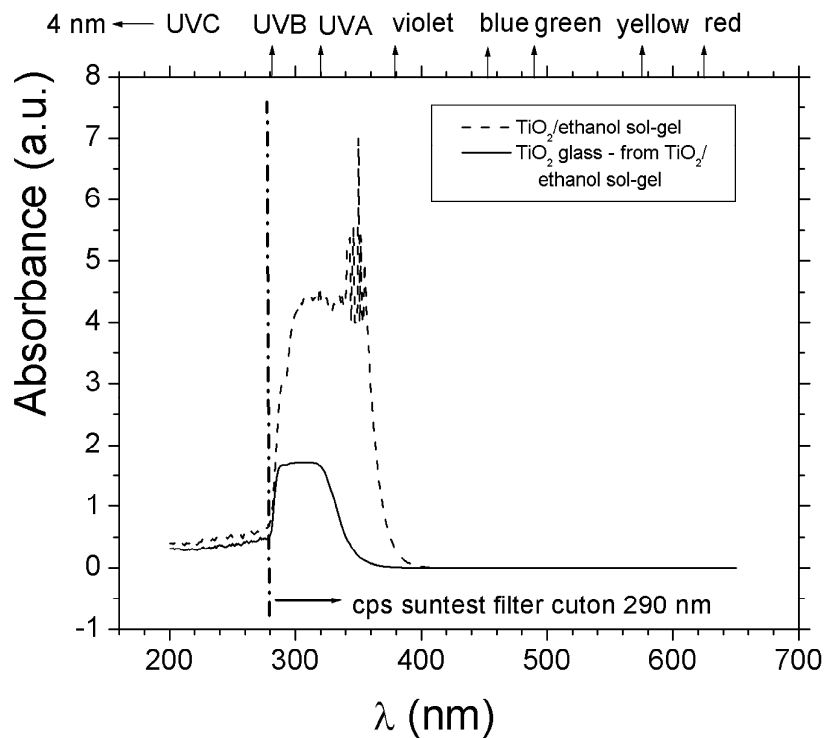

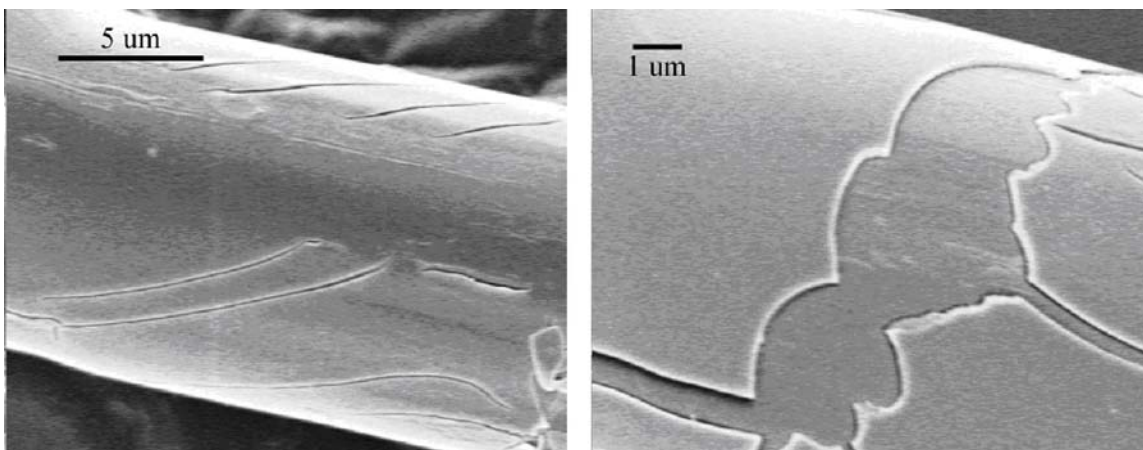Figure 4.12: UV-Vis absorption of TiO$_2$ sol-gel and dried glassy TiO$_2$ film.

Figure 4.13: SEM of TiO_2 coating showing a thin film with thickness on the order of ~100's of nanometers.

Compaction of Fiber Microstructure

In Chapter 3 exposure to water was shown to result in physical separation of the fibrillar elements within the PBO fiber. In particular the size of voids between the fibrils was found to increase. SEM evidence indicated that the presence of concentrated phosphoric acid accelerates this swelling and separation perhaps due to the effects of a synergistic chemical reaction. Because the loss of strength is primarily due to loosening of the fiber morphology there may be an opportunity to improve the properties of PBO. Any post spinning process that compacts the structure of the fiber, increases the size of the fibrillar elements and/or reduces the volume fraction of voids should be a route to improving the mechanical properties. Three possible approaches are: using twist to compact the fibrillar morphology of the fiber and enhance load transfer between fibrils, using hydrostatic pressure to compact the fibrillar morphology, and using tension and the plasticizing influence of CO_2 to align crystalline domains and decrease the number of defects in the crystalline material.

The initial idea here is to increase the strength of single filament by an interlocking mechanism where the fibrils are held together by radial force and friction due to twist. Fibrils in the twisted fiber can break more than once and still support load via load transfer from fibril to adjacent fibril. There should be an optimum twist since very high degree of twist will result in a transverse compression stress on fibrils and a decrease in strength.

In the tensile results for twisted single fibers presented in Figure 4.13, the load-at-break of PBO fibers increases very slightly for degree of twist of less than ~5 turns. After 5 turns the tenacity no longer increases and begins to show significantly increased variability.

In the previously described experiments using $scCO_2$ to extract residual phosphoric acid, fibers were placed under hydrostatic pressure using $scCO_2$ fluid. Figure 4.3 shows a weak trend of an increase in fiber strength for pressures of 2500 and 3250 psi at a temperature of 100°C. This result encouraged a further look at using $scCO_2$ in

combination with hydrostatic stress to compact and increase the perfection of the fiber morphology. Experiments were conducted in which $scCO_2$ and nitrogen was used to apply hydrostatic pressure to the fiber with silicon oil as an intermediate fluid. Fibers were placed in a pressure vessel filled with silicon oil and hydrostatic pressure was applied using both nitrogen gas and $scCO_2$. Conditions of temperature and pressure were in both cases 5000 psi and 100°C. Figure 4.15 shows the results of tensile testing for these fibers. The indication is that there is no increase in fiber tenacity with such treatment, and in fact there is a drop for the fibers with $scCO_2$. Figure 4.16 shows SEM micrographs of the PBO AS fiber surface after pressure treatment in silicon oil. It appears that the silicon oil, which is highly soluble in $scCO_2$, has completely wet the surface and being of low molecular weight may have swollen the fiber.

Tension, usually combined with heat, is widely used in fiber industry to increase the orientation of both amorphous and crystalline region of fibers. There are two competitive processes during this: fibers tend to become oriented upon tension and lose orientation on heating. If the magnitude of tension is adequate to overcome the influence toward disorder then the crystalline material is forced to align and the heat can have the effect of increasing the perfection of the crystalline material. This is precisely the approach used to manufacture high modulus PBO (PBO HM) fibers from PBO AS fiber. In this work $scCO_2$ is used with the idea that it may partially plasticize the fiber material and enable a decrease in the defects present.

The effect of tension on fiber properties was explored by placing fibers under tension of ~40 cN or approximately ~80% of the fiber breaking strength. Experiments were conducted in both air at standard pressure and temperature and in sub critical CO_2 at 20 °C and 5000 psi for a 24 hour duration. The results of tensile testing on fibers treated in this way are shown in figure 4.17. The fiber placed under tension in air shows the same tenacity as control fibers not held under tension. The fiber held under tension in the $scCO_2$ environment shows a slight increase in tenacity but given the large degree of variability this is not a significant effect.

All three of these approaches to compact the fiber morphology and decrease defects using mechanical means of twist, hydrostatic pressure and tension combined with $scCO_2$ conditions resulted in no significant increase in fiber tenacity. One possible explanation for this may be that even if a compacting force is applied to the fiber, once that force is removed the comparatively weak van der Waals inter-fibril and dipole inter-chain forces are insufficient to maintain the compacted morphology. The observation of little or no increase in properties with application of a compacting force in the presence of $scCO_2$ suggests that $scCO_2$ has little effect on the number of defects present in PBO fibers.
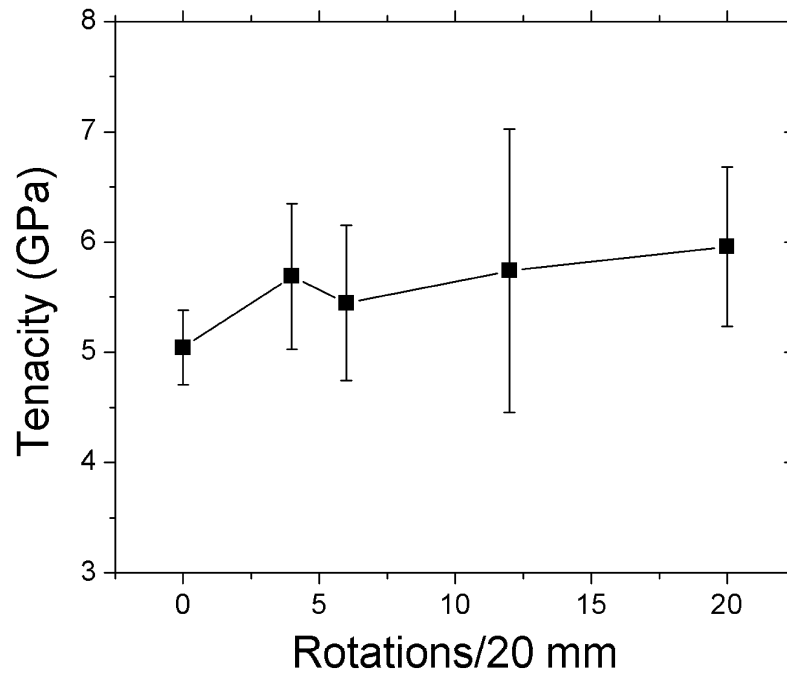
Figure 4.14: Tensile testing results showing effect of twist on fiber tenacity. Error bars indicate 1 standard deviation on the mean.
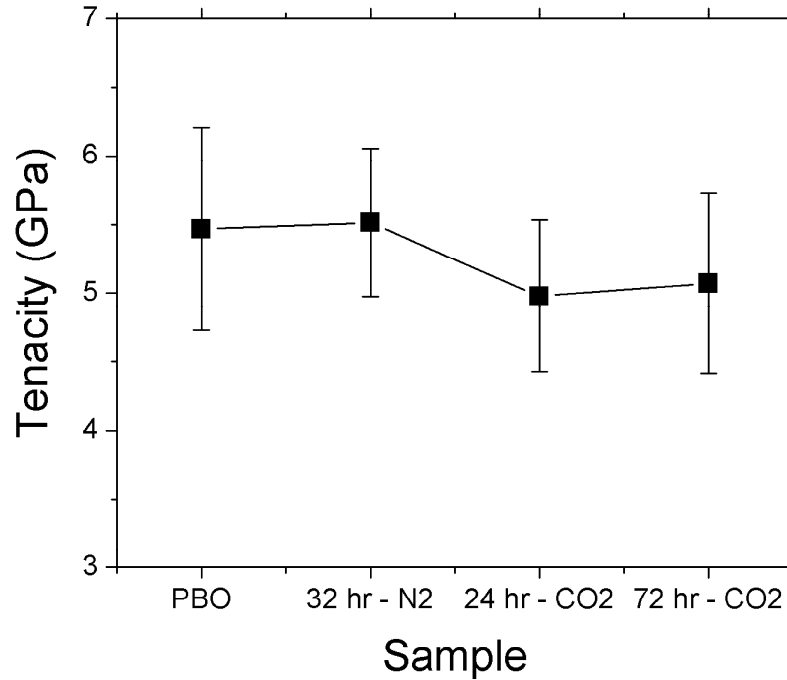

Figure 4.15: Tensile testing results showing effect of hydrostatic pressure on fiber tenacity
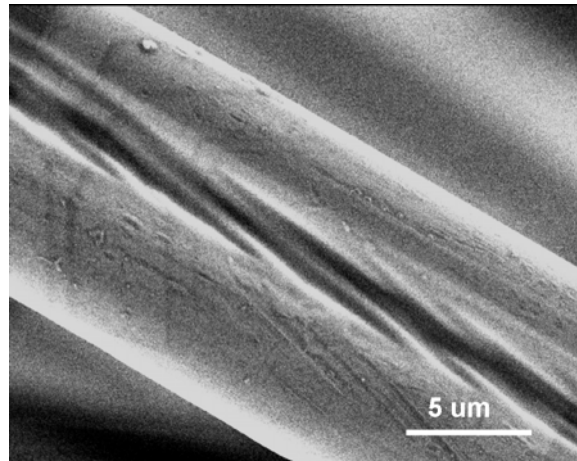
Figure 4.16: SEM micrographs of PBO AS fiber surfaces after compaction in scCO$_2$ and silicon oil.
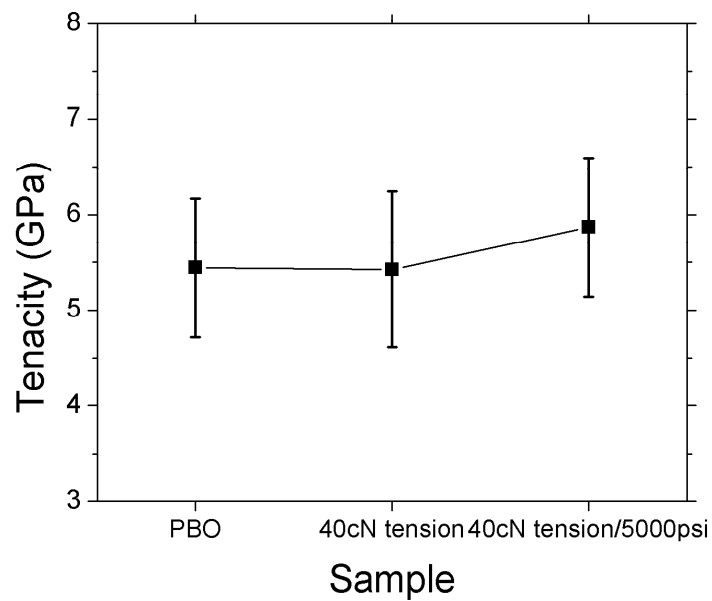

Figure 4.17: Tensile testing results showing effect comparing the tenacity of untreated PBO AS fiber with PBO AS fiber held at 40cN tension and PBO AS fiber held at 40 cN tension and soaked in a sub-critical CO$_2$ environment under 5000 psi hydrostatic pressure. Error bar indicate 1 standard deviation on the mean.
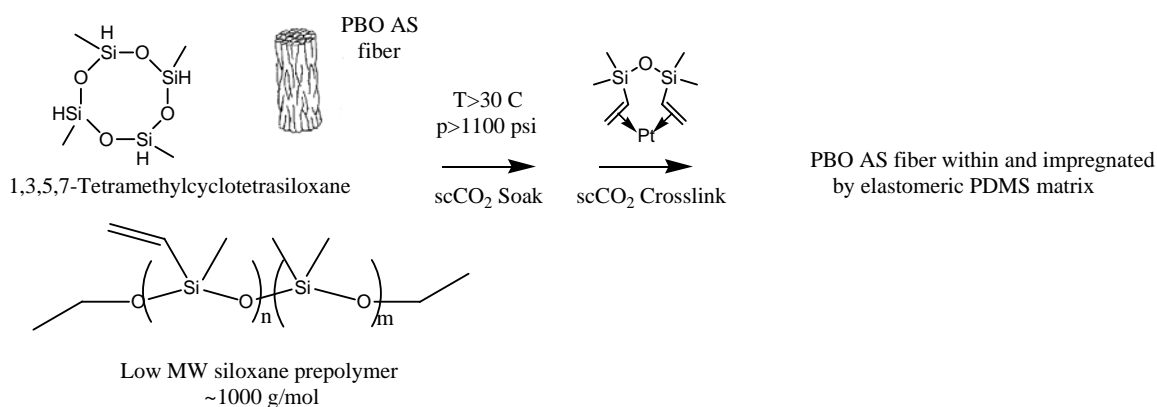
Super-critical Fluid Approach to PBO AS/Polysiloxane Composites

The results of Chapter 3 indicate that the degradation of PBO AS fiber properties by moisture is primarily due to non-recoverable loosening of the fiber structure and introduction of larger number and size defects. In the previous section increases in fiber tenacity are observed due to compaction of the fiber microstructure using twist and hydrostatic pressure applied by $scCO_2$. These results suggest that if the fibrillar microstructure could be compacted and a secondary inter-fibril force added to maintain the compaction, both the initial fiber tenacity and resistance to degradation by moisture might be improved.

Composites of PBO AS fiber and polysiloxanes crosslinked in a hydrosilation reaction have been prepared in super-critical carbon dioxide environment according to Scheme 4.4. This approach takes advantage of the high solubility of siloxanes in $scCO_2$ by introducing relatively small molecular weight vinyl substituted polysiloxane prepolymer and 1,2,5,7-Tetramethylcyclotetrasiloxane ($D4^H$) crosslinker to the fiber, swelling the fiber with them and subsequently initiating crosslinking by introduction of a platinum catalyst. The intent is that the resulting elastomeric PDMS will infiltrate the fiber, adhere to the fibrillar elements and provide a robust secondary force to prevent expansion of the fiber microstructure by exposure to liquid and vapor phase water.

Two polysiloxane resins systems were investigated: the first is a low molecular weight vinyl substituted polysiloxane prepared in a polycondensation reaction (PVMS) and the second is a commercially available PDMS resin system with higher molecular weight (Sylgard 184).

Scheme 4.4: Preparation of PBO AS/crosslinked PDMS Composites in $scCO_2$ environment

1,3,5,7-Tetramethylcyclotetrasiloxane

T>30 C
p>1100 psi

$scCO_2$ Soak $scCO_2$ Crosslink

PBO AS fiber within and impregnated by elastomeric PDMS matrix

Low MW siloxane prepolymer
~1000 g/mol

Preparation of Vinyl Substituted PVMS prepolymer

The PVMS prepolymer was prepared according to scheme 4.1, a polycondensation of dichlorodimethylsilane with dichloromethylvinylsilane. After the initial reaction the majority of the aqueous phase was removed, zinc acetate added and heat applied to decrease the cyclic content and increase molecular weight. The

prepolymer was then washed in absolute ethanol to end cap any active chain ends and remove the remaining hydrochloric acid polycondensation product.

Figure 4.18 shows the NMR spectra of the prepolymer material. The group of peaks at ~6 ppm shift are associated with the vinyl protons while the large peak at ~0 ppm is associated with methyl protons. The peaks at ~3.7 ppm, ~1.5 ppm and ~1.2 ppm are attributed to acetone, water and ethanol impurities respectively. Integration and comparison of the vinyl and methyl proton peaks indicates a ratio of methylvinyl to dimethyl repeats of approximately 1:10.

MALDI-TOF was used to characterize the molecular weight of the PVMS product [27]. The distribution is shown in Figure 4.19. The mass spectrum shows a series of four distributions of ions between m/z 500 to m/z 2000 all of which have a m/z spacing of approximately 74 corresponding to the mass of a polydimethylsiloxane repeat unit. The four distinct distributions indicate that the PVMS prepolymer is probably a mixture of cyclic and linear species. The number average molecular weight is calculated to be 1003 g/mol yeilding an average chain length of approximately 13.5 units containing on average 1.4 vinyl substituted repeat units each. Density of the liquid was estimated to be 1.179 g/ml.
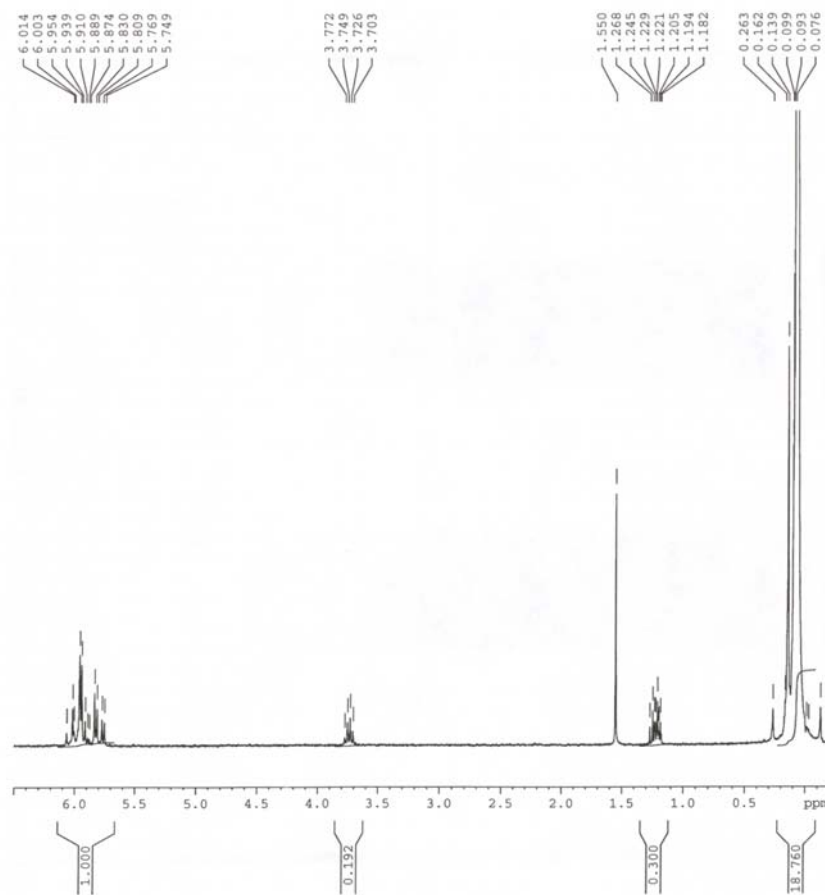

Figure 4.18: NMR spectra of vinyl substituted PDMS prepolymer. Peaks near 6 ppm shift are associated with vinyl protons, peaks near 0 ppm are associated with methyl protons. Integration indicates a 13.5:1 ratio of dimethyl siloxane repeats to methylvinyl siloxane repeats. Peak near 1.5 ppm is water.
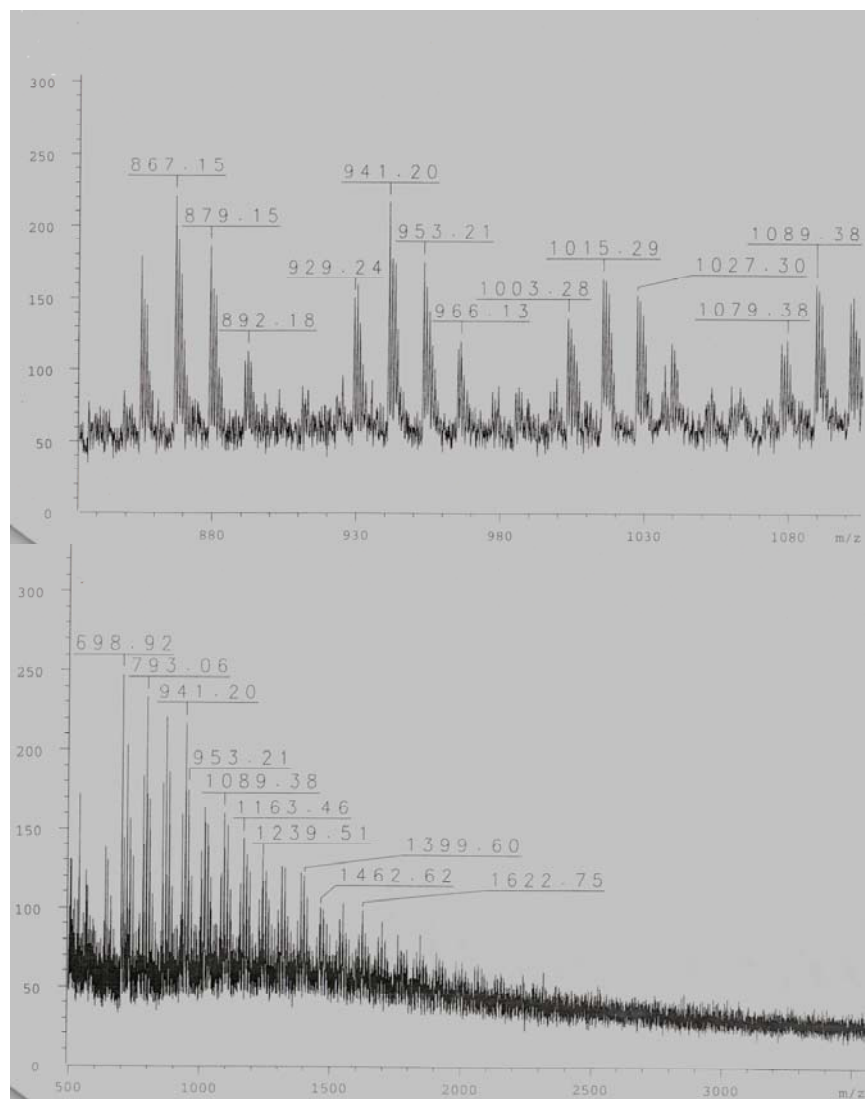
Figure 4.19: MALDI-TOF molecular weight distribution for vinyl substituted PDMS prepolymer. M_n is 1003 g/mol.

Polymerization of PBO AS/Crosslinked PDMS composites in scCO$_2$

On the basis of the PVMS prepolymer NMR and MALDI-TOF results the PVMS prepolymer was combined with an appropriate quantity of the D4^H crosslinker such that there was an approximately 1:1 ratio of vinyl groups to D4^H hydrides. The PBO AS fiber and PVMS prepolymer/D4^H mixture was soaked in scCO$_2$ at 50 °C under pressures of 1500 psi, 2500 psi and 3500 psi for 4 hours. The pressure vessels were depressurized to initiate crosslinking by the addition of Karstedt's catalyst then re-pressurized to T=50 °C, 1500 psi, 2500 psi and 3500 psi. The cross-linking reaction was complete in less than two

hours and the vessels were slowly depressurized over 0.5 hours using the ER-3000 controller.

Identical procedures and process conditions were used with the Sylgard 184 PDMS resin and catalysis was accomplished using 5 wt% of the Sylgard 184 crosslinker. The crosslinking reaction in this case took less than 30 minutes and yielded a relatively stiffer elastomeric product.

SAXD was used to determine what effect cross-linked polysiloxane had on the fiber morphology. Figure 4.20 compares the control fiber diffraction patterns with those of the PBO AS/PVMS composite prepared at each pressure condition. As described previously in Chapter 3 the equatorial streak is known to be due to scattering by needle-like voids oriented along the fiber axis [12]. The composite fiber diffractions contain the same equatorial streak but also show an amorphous halo that might be associated with either particles of PDMS or cavities created by foaming upon the release of CO_2 pressure. The Guinier correlation lengths of the equatorial streak *($D_{Equatorial}$)* and diffuse halo *($D_{Meridonal}$)* are tabulated in Table 4.2 assuming the equatorial streak is scattering from cylindrical voids and the diffuse halo to spherical particles. The decrease in $D_{Equatorial}$ with increasing polymerization pressure is associated with a decrease in the radius of gyration of the longitudinal voids present in the PBO AS fiber. There is also a weak trend of decreasing $D_{Meridonal}$ with process pressure. Similar results SAXD results for Sylgard 184 are shown in figure 4.21 and Table 4.3.

These results are consistent with infiltration of the fiber by crosslinked polysiloxane; first the fiber was compressed by the high pressure conditions of polymerization, secondly upon crosslinking the polysiloxane will decrease in volume. The decreasing correlation lengths infer that the polysiloxane is preventing expansion of the fiber once the process pressure is released.
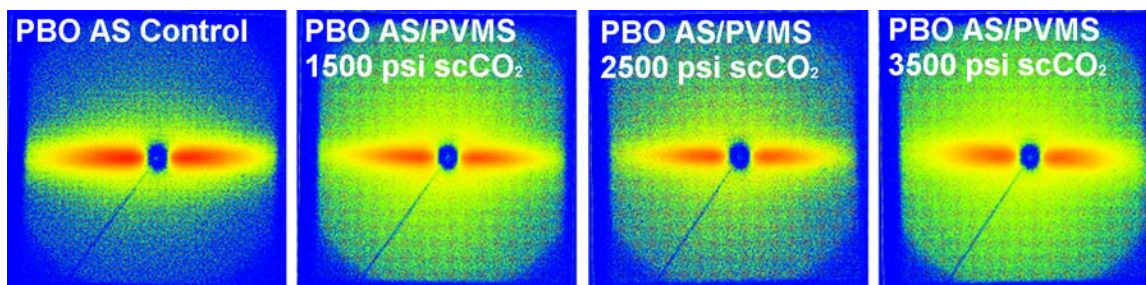

Figure 4.20: SAXD diffraction pattern for PBO AS control fibers compared to PBO AS/crosslinked PVMS composites fabricated in scCO$_2$.

Table 4.2: Change in equatorial and meridonal Guinier correlation length with increasing scCO$_2$ fluid pressure for PBO AS/vinyl substituted prepolymer PDMS composites fabricated in scCO$_2$

	$D_{Equatorial}$ (nm)	$D_{Meridonal}$ (nm)
PBO AS control fiber	3.60	1.16
PBO AS/Vinyl sub'd PDMS ScCO$_2$: 1500 psi/50 C	3.23	1.07
PBO AS/Vinyl sub'd PDMS ScCO$_2$: 2500 psi/50 C	3.15	1.01
PBO AS/Vinyl sub'd PDMS ScCO$_2$: 3500 psi/50 C	3.17	1.03

SEM micrographs PBO AS control fibers are shown in Figures 4.22 and 4.23. The fibbrillar structure of the fiber can be clearly discerned by the striations on the fiber surface and by the fibrillation evident near kink bands. Figure 24 shows a fiber surface and kink band for a fiber scCO2 fluid soaked in crosslinked PVMS. The polysiloxane has wetted the surface well though there still appears to be splitting and fibrillation of the fiber near kink bands. Figure 4.25 shows a kink band on a fiber scCO2 fluid soaked in crosslinked Sylgard 184. Again the surface appears to have been wetted by the siloxane fluid. Fibrillation near the kink band does not appear to have been inhibited.

Although there is no direct visual evidence of siloxane impregnation of the fiber in the SEM results the Siloxaanes do wet the surfaces of the fiber very well. The length scale of the voids between fibrillar elements is less than 10 nm so would not expect to see changes using the SEM technique. The SAXD diffraction data are a strong indication that both the polysiloxane prepolymers used do infiltrate the fiber and add secondary inter-fibril forces that tend to maintain compaction imposed during crosslinking.
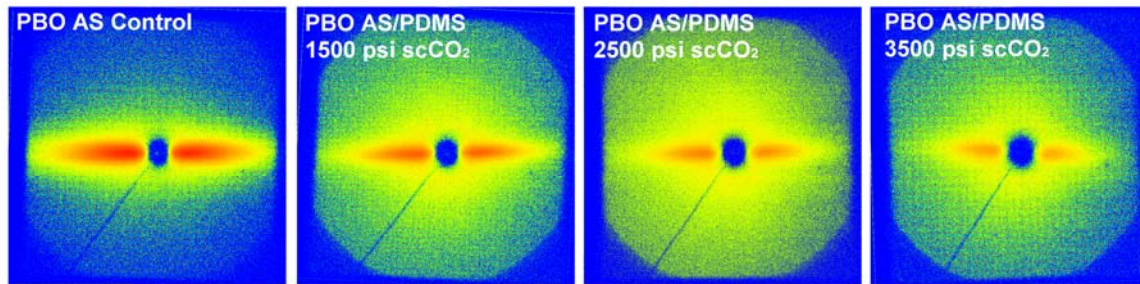

Figure 4.21: SAXD diffraction pattern for PBO AS control fibers compared to PBO AS/Sylgard 184 PDMS composites fabricated in scCO$_2$

Table 4.3: Change in equatorial and meridonal Guinier correlation length with increasing scCO$_2$ fluid pressure for PBO AS/Sylgard 184 PDMS Composites fabricated in scCO$_2$.

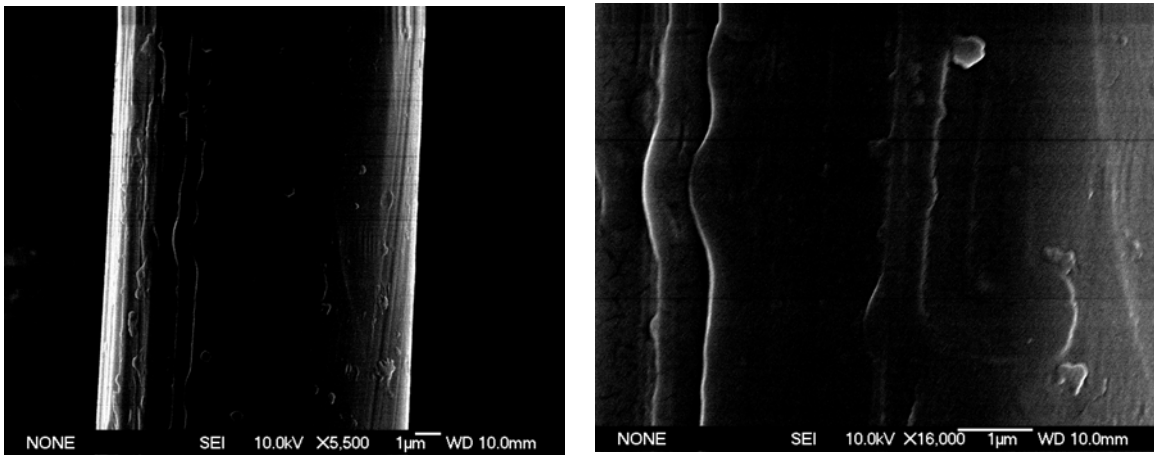|	$D_{Equatorial}$ *(nm)*	$D_{Meridonal}$ *(nm)*
PBO AS control fiber	3.60	1.16
PBO AS/Sylgard 184 PDMS ScCO$_2$: 1500 psi/50 C	3.16	1.13
PBO AS/Sylgard 184 PDMS ScCO$_2$: 2500 psi/50 C	3.03	1.11
PBO AS/Sylgard 184 PDMS ScCO$_2$: 3500 psi/50 C	2.93	1.10

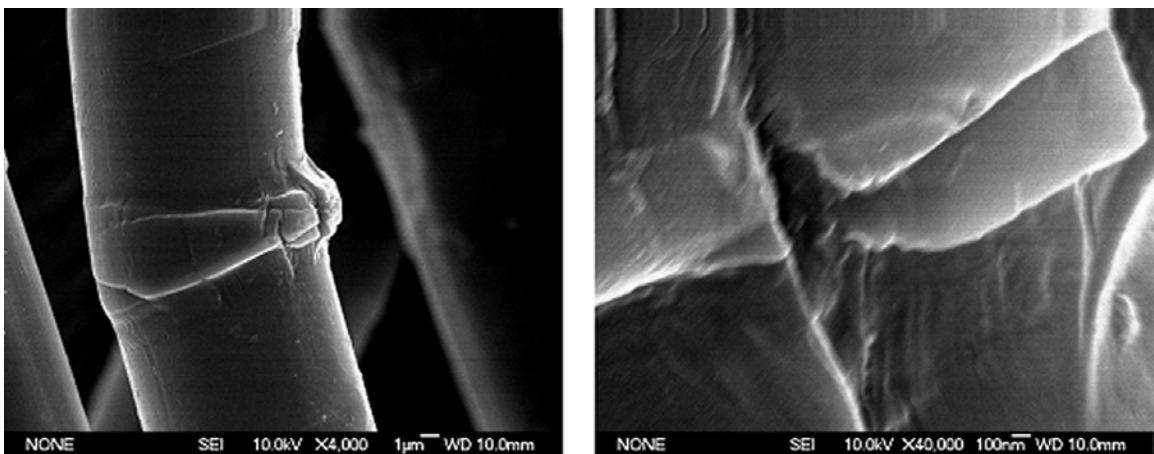Figure 4.22: SEM micrographs of PBO AS control fiber surfaces

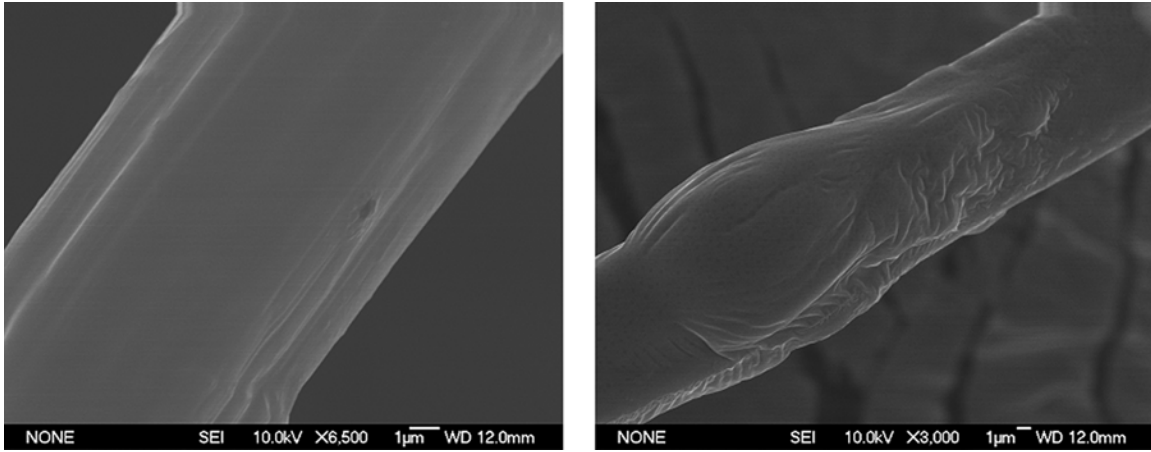Figure 4.23: SEM micrograph of PBO AS control fiber kink bands

Figure 4.24: SEM micrograph of PBO AS fiber surfaces after soaking and crosslinking of PVMS monomer in $scCO_2$ environment. P=1500 psi, T=50 C.
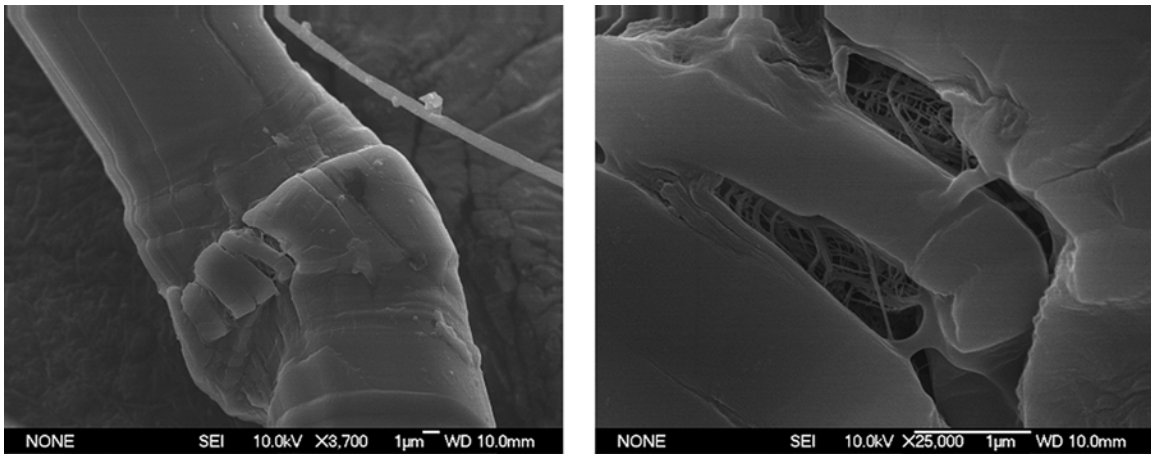

Figure 4.25: SEM images of PBO AS fiber kink band after soaking and crosslinking of Sylgard 184 PDMS in $scCO_2$ environment. P=1500 psi, T=50 C.

Conclusions

In light of the potential of residual phosphoric acid to either react with the oxazole ring of the PBO mer and/or attract water into the fiber super critical CO_2 extraction was used as a means of removal. Elemental analysis shows that the weight % of phosphorus present in the PBO fibers was reduced from 0.4% for neat PBO AS fiber to 0.25% for $scCO_2$ washed fiber. Mechanical testing showed that the $scCO_2$ extraction process did not degrade the fiber mechanical properties and in fact showed a weak trend to increase fiber tenacity. The high pressure and relatively high temperatures used during the $scCO_2$ extraction process may have the effect of compacting the fiber and decreasing the number and size of defects.

A second approach to the problem of residual phosphoric acid was to introduce a small molecule with a pKa value chosen such that it might complex with residual phosphoric acid and then be removed using $scCO_2$ extraction. Fibers exposed to a series of weakly basic small molecules: trimethyl phosphate, pyridine and morpholine showed no initial reduction in strength, however subsequent exposure to UV-Vis spectrum light showed these compounds to have a significant detrimental effect on UV-Vis stability of PBO fibers. ATR-FTIR spectroscopy on the treated fibers prior to UV-Vis indicated that exposure to these small molecules in aqueous conditions resulted in chemical degradation at the fiber surface.

UV-Vis stabilization of PBO fibers was attempted using UV blocking or absorbing materials to protect the fiber surface. Fibers were coated with both carbon black powder and exfoliated graphite flakes. Mechanical testing of coated fibers exposed to UV-Vis radiation and observation of the coated fiber surface by SEM shows that UV-Vis stability was not enhanced due to imperfect coverage of the fiber surface. A second attempt at UV-Vis stabilization was made using a glassy titanium dioxide coating made by dip coating fibers in a sol-gel precursor solution. SEM revealed that thin coatings of glassy titanium dioxide with thickness on the order of 100 nm were achieved. The material does absorb strongly in the UVB region but mechanical testing of TiO_2 coated fibers exposed to UV-Vis radiation showed no improvement in UV-Vis stability. The failure of this coating material is due shrinkage and subsequent breaks in coverage occurring as the solvent was driven out of the sol-gel to form the glassy TiO_2 coating. In addition the glassy TiO_2 material lacks enough compliance to accommodate bending of the fibers leading to fracture of the coating when the fiber is handled.

The finding that degradation by moisture exposure is primarily due to physical separation of the fibrillar elements (Chapter 3) suggests that any process resulting in compaction of the fibrillar bundle may improve the fiber properties. Several approaches were undertaken. Twist was applied to the fibers to apply the compacting force. Single fiber tensile testing showed moderate increase in tensile strength. Fibers were exposed to hydrostatic pressure in nitrogen and CO_2 at room temperature. No increases in strength were observed. Fibers were placed in tension to 60% of fiber breaking load and exposed to hydrostatic pressure in $scCO_2$. Again a weak trend toward increase in fiber properties was observed.

Composites of PBO AS fiber and polysiloxanes crosslinked in a hydrosilation reaction have been prepared in super-critical carbon dioxide environment. This approach takes advantage of the high solubility of siloxanes in $scCO_2$ to swell the fiber with low

molecular weight vinyl substituted polysiloxane resin and crosslinker. Crosslinking by hydrosilation was initiated by introduction of a platinum catalyst. The intent is that the elastomeric PDMS phases will adhere to the fibrillar elements and provide a secondary inter-fibrillar force able to prevent expansion of the fiber by moisture.

Two siloxane prepolymer systems were evaluated. The first was a vinyl substituted PDMS prepared from dichlorodimethylsilane and dichloromethylvinylsilane in a polycondensation reaction to form a mixture of linear and cyclic siloxane species with a ratio of 10:1 dimethylsiloxane to vinylmethylsiloxane repeats and number average molecular weight of 1000 g/mol. The second was Sylgard 184 a commercially produced PDMS resin that was also crosslinked in a hydrosilation reaction.

SAXD results for both PBO AS fiber/Crosslinked PDMS composite systems indicate a reduction in the radius of gyration of the longitudinal voids present in the PBO AS fiber. The reduction in void size is consistent with infiltration of the fiber by the PDMS materials in two ways; during crosslinking the fiber is compacted by the super-critical fluid pressure and upon crosslinking the PDMS undergoes a reduction in volume. The observation of reduced void size after crosslinking and depressurization implies that the crosslinked PDMS has introduced a secondary inter-fibril force capable of maintaining fiber compaction. In addition SAXD of the composite systems displays diffuse scattering that may be due to the formation of PDMS particles or foaming of the PDMS upon release of the super-critical fluid pressure.

Comparison of SEM micrographs of PBO AS control fibers and PBO AS/Crosslinked PDMS indicate the polysiloxanes do wet the fiber surface. Unsurprisingly, as the length scale of the void spaces anticipated to be accessible under super-critical carbon dioxide is less than 10 nm, there is no direct visual evidence in the SEM results of swelling of the PBO AS fiber by crosslinked siloxane.

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